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Synthesis of chiral 2,3-*cis*-fused butan-4-olides from levoglucosenone–1,3-diene Diels–Alder adducts

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Experimental

The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were recorded using Bruker AM-300 (300 MHz for ^{1}H and 75.47 MHz for ^{13}C) and Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C) instruments. IR spectra were recorded on spectrophotometers Shimadzu IRPrestige-21 or Bruker Tensor 27 (from films or mulls in mineral oil). Mass spectra were measured on a GC-MS instrument Hewlett Packard, chromatograph HP 6890 with a mass-selective detector HP 5973. Optical rotation was determined on a polarimeter Perkin Elmer-341. Analytical TLC was carried out on Sorbfil plates of the grade PTSKh-AF-A (”Sorbpolymer” Co., Krasnodar). The melting points were measured on a Boëtius 05 heating block.

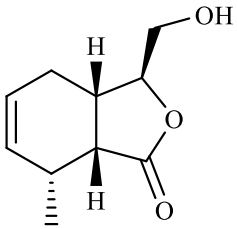
General procedure.

Method A. To a solution of adduct **1a-f** (1 mmol) in *i*-PrOH (5 ml) was added 30% H_2O_2 (0.51 ml, 5 mmol), H_2SO_4 (0.005 ml, 0.1 mmol) and the resulting solution was stirred at 80^{o}C. After completion of the reaction (TLC), the mixture was cooled to room temperature and treated with a saturated solution of Na_2SO_3 until peroxide compounds disappeared. The solvent was removed under reduced pressure, and the aqueous phase was extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated under vacuum and purified by silica gel column chromatography.

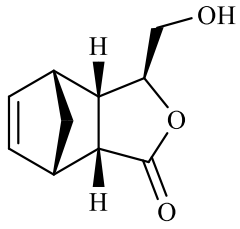
Method B. To a solution of adduct **1a-f** (1 mmol) in *i*-PrOH (5 ml) was added 30% H_2O_2 (0.51 ml, 5 mmol), $TsOH{\cdot}H_2O$ (19 mg, 0.1 mmol), and the resulting solution was stirred at 80^{o}C. After completion of the reaction (TLC), the mixture was cooled to room temperature and treated with a saturated solution of Na_2SO_3 until peroxide compounds disappeared. The solvent was removed under reduced pressure, and the aqueous phase was extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated under vacuum and purified by silica gel column chromatography.

Method C. To a solution of adduct **1a-f** (1 mmol) in *i*-PrOH (5 ml) was added 30% H_2O_2 (0.51 ml, 5 mmol), 85%-H_3PO_4 (0.08 ml, 1.2 mmol) and the resulting solution was stirred at 80^{o}C.

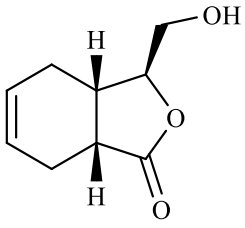
After completion of the reaction (TLC), the mixture was cooled to room temperature and treated with a saturated solution of Na_2SO_3 until peroxide compounds disappeared. The solvent was removed under reduced pressure, and the aqueous phase was extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated under vacuum and purified by silica gel column chromatography.



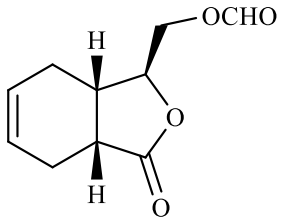
(3S,3aS,7R,7aR)-3-Hydroxymethyl-7-methyl-1,3,3a,4,7,7a-hexahydro-2-benzofuran-1-one **2a**. White crystals, mp 105-110ºC, $[\alpha]_D^{20}$-31.8º (*c* 1.0, $CHCl_3$), R_f 0.5 (hexane-EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 3466, 2850, 1751, 1460, 1365, 1197, 1031. ^{1}H NMR (C_6D_6) δ: 1.22 (d, 3H, CH_3, *J* 7.24 Hz), 2.02 (ddd, 1H, CH_2, *J* 16.67, 4.09, 2.83 Hz), 2.23 (ddd, 1H, CH_2, *J* 16.67, 7.23, 1.58 Hz), 2.7 (m,1H, CH), 2.78 (m,1H, CH), 2.89 (tdd,1H, CH, *J* 7.24, 2.83, 2.2 Hz), 3.52 (dd,1H, CH_2, *J* 12.58, 3.46 Hz), 3.56 (dd, 1H, CH_2, *J* 12.58, 2.2 Hz), 4.02 (m, 1H, CH_2, *J* 3.46, 2.2 Hz), 5.54–5.56 (m, 2H, CH=). ^{13}C NMR ($CDCl_3$) δ: 17.21 (CH_3), 25.06 (C^4), 28.48 (C^7), 34.56 (C^{3a}), 43.51 (C^{7a}), 63.02 ($C^{1'}$), 86.02 (C^3), 125.39 (C^5), 133.93 (C^6), 178.26 (CO). MS, *m/z*: 182.0937 $[M]^+$. Calc. for $C_{10}H_{14}O_3$: 182.0943.



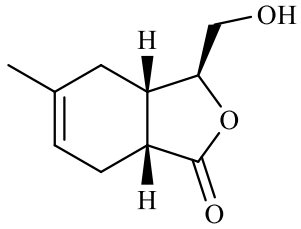
(1S,2R,5S,6S,7R)-5-Hydroxymethyl-4-oxatricyclo-[5.2.1.0^{2,6}]dec-8-en-3-one **2b**. White crystals, mp 96-97ºC, $[\alpha]_D^{20}$-51.8º (*c* 1.0, $CHCl_3$), [ref[1]: mp 96-97ºC, $[\alpha]_D^{26}$-49.77º (*c* 1.01, $CHCl_3$)]. R_f 0.4 (hexane-EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 2974, 1752, 1351, 1215, 1086, 1016, 739. ^{1}H NMR ($CDCl_3$) δ: 1.45 (d, 1H, H^{10a}, *J* 8.5 Hz), 1.65 (d, 1H, H^{10b}, *J* 8.5 Hz), 2.18 (br.s, 1H, OH), 2.93 (ddd,1H, H^6, *J* 8.2, 3.7, 3.1 Hz), 3.13 (m,1H, H^7), 3.30 (dd, 1H, H^2, *J* 8.2, 4.5 Hz), 3.30 (m,1H, H^1), 3.61 (dd, 1H, H^{11a}, *J* 12.1, 4.4 Hz), 3.78 (dd, 1H, H^{11b}, *J* 12.1, 3.1 Hz), 4.40 (dt, 1H, H^5, *J* 12.1, 3.1, 3.1 Hz), 6.25 (dd, 1H, H^8, *J* 5.7, 2.9 Hz), 6.30 (dd, 1H, H^9, *J* 5.7, 2.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 42.54 (C^6), 45.42, 45.65, 48.66 (C^1, C^2, C^7), 51.55 (C^{10}), 64.37 (C^{11}), 83.09 (C^5), 134.68, 136.48 (C^8, C^9), 178.54 (C^3). MS, *m/z*: 180.0781 $[M]^+$. Calc. for $C_{10}H_{12}O_3$: 180.0786.



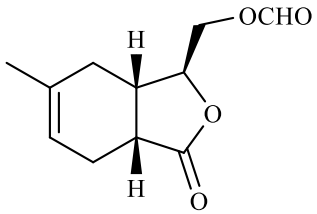
(3S,3aS,7aR)-3-Hydroxymethyl-1,3,3a,4,7,7a-hexahydro-2-benzofuran-1-one **2c.** Colourless oil. $[\alpha]_D^{20}$-12.2º (*c* 1.0, $CHCl_3$), [ref[2]: $[\alpha]_D^{20}$-6.5º (*c* 2.9, $CHCl_3$)]. R_f 0.4 (hexane-EtOAc, 1:1).). IR ($CHCl_3$, ν/cm^{-1}): 2917, 1766, 1437, 1365, 1177, 1037, 937, 671. ^{1}H NMR ($CDCl_3$) δ: 1.93 (m, 1H, H^4), 2.20-2.40 (m, 3H, H^4, H^7), 2.65 м (1H, H^{3a}), 2.82 (br.s, 1H, OH), 2.93 (td, 1H, H^{7a}, *J* 6.7, 8.5), 3.69 (dd, 1H, CH_2OH, *J* 12.4, 4.6 Hz), 3.87 (dd, 1H, CH_2OH, *J* 12.4, 2.9 Hz), 4.20 (dt, 1H, H^5, *J* 4.6, 2.9, Hz), 5.80 (m, 2H, H^5, H^6). ^{13}C NMR ($CDCl_3$) δ: 22.13 (C^4), 24.66 (C^7), 33.31 (C^{3a}), 37.24 (C^{7a}), 62.49 (CH_2OH), 85.46 (C^3), 125.41, 125.83 (C^5, C^6), 180.07 (C^1). MS, *m/z*: 168.0780 $[M]^+$. Calc. for $C_9H_{12}O_3$: 168.0786.



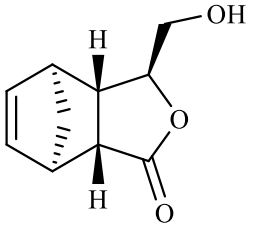
(3S,3aS,7aR)-3-Formyloxymethyl-1,3,3a,4,7,7a-hexahydro-2-benzofuran-1-one **2'c**. Colourless oil. $[\alpha]_D^{20}$+6.8º (*c* 1.0, $CHCl_3$), [ref[3]: $[\alpha]_D^{27}$+14.5º (*c* 1.0, $CHCl_3$)]. R_f 0.45 (hexane-EtOAc, 2:1). IR ($CHCl_3$, ν/cm^{-1}): 2946, 1768, 1726, 1440, 1366, 1167, 1059, 937, 757. ^{1}H NMR ($CDCl_3$) δ: 2.00 (m,1H, H^7), 2.25-2.45 (m, 3H, H^4, H^7), 2.59 (m,1H, H^{7a}), 2.91 (td, 1H, H^{3a}, *J* 6.8, 8.1 Hz), 4.28 (dd, 1H, CH_2O, *J* 11.4, 5.0 Hz), 4.32 (m, 1H, H^1), 4.41 (dd, 1H, CH_2O, *J* 11.4, 2.9 Hz), 5.81 (m, 2H, H^5, H^6). ^{13}C NMR ($CDCl_3$) δ: 22.24 (C^4), 24.50 (C^7), 34.15 (C^{3a}), 36.80 (C^{7a}), 63.35 (CH_2OH), 81.87 (C^3), 125.13, 126.06 (C^5, C^6), 160.32 (CHO), 178.47 (C^1). MS, *m/z*: 196.0731 $[M]^+$. Calc. for $C_{10}H_{12}O_4$: 196.0736.



(3S,3aS,7aR)-3-Hydroxymethyl-5-methyl-1,3,3a,4,7,7a-hexahydro-2-benzofuran-1-one **2d**. Colourless oil. $[\alpha]_D^{20}$-24.2º (*c* 1.0, $CHCl_3$). R_f 0.4 (hexane-EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 2929, 1766, 1439, 1368, 1189, 1155, 1040, 754. ^{1}H NMR ($CDCl_3$) δ: 1.70 (d, 3H, Me, *J* 1.5 Hz), 1.83 (dd, 1H, H^4, *J* 17.2, 4.1 Hz), 2.18 (dd, 1H, H^4, *J* 17.2, 7.1 Hz), 2.26-2.35 (m, 2H, H^7), 2.68 (m, 1H, H^{3a}), 2.86 (td, 1H, H^{7a}, *J* 6.8, 8.6 Hz), 3.70 (dd, 1H, CH_2OH, *J* 12.5, 4.9 Hz), 3.88 (dd, 1H, CH_2OH, *J* 12.5, 3.1 Hz), 4.15 (dt, 1H, H^5, *J* 4.9, 3.1, Hz), 5.51 (ddd, 1H, H^6, *J* 5.7, 2.8, 1.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.87 (C^4), 23.62 (Me), 27.84 (C^7), 34.08 (C^{3a}), 37.17 (C^{7a}), 62.67 (CH_2OH), 85.41 (C^3), 119.35(C^6), 133.12 (C^5), 180.18 (C^1). MS, *m/z*: 182.0937 $[M]^+$. Calc. for $C_{10}H_{14}O_3$: 182.0943.

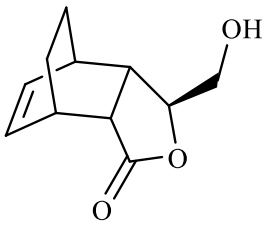


(3S,3aS,7aR)-3-Formyloxymethyl-5-methyl-1,3,3a,4,7,7a-hexahydro-2-benzofuran-1-one **2'd.** Colourless oil. $[\alpha]_D^{20}$+3.5º (*c* 0.81, $CHCl_3$). R_f 0.44 (hexane-EtOAc, 3:1). IR ($CHCl_3$, ν/cm^{-1}): 2960, 2917, 1777, 1729, 1446, 1173, 937. ^{1}H NMR ($CDCl_3$) δ: 1.67 (s, 3H, CH_3), 1.88 (dd, 1H, H^7, *J* 17.1, 4.4), 2.22 (dd, 1H, H^7, *J* 17.1, 7.2), 2.34 (m, 2H, CH_2), 2.60 (m, 1H, H^{7a}), 2.88 (ddd, 1H, H^{3a}, *J* 8.1, 7.0, 7.0), 4.28 (m, 2H, $H^{1'}$, H^1), 4.40 (m, 1H, $H^{1'}$), 5.50 (m, 1H, H^5), 8.08 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$) δ: 22.67 (C^7), 23.54 (CH_3), 29.55 (C^4), 34.69 (C^{7a}), 36.48 (C^{3a}), 63.25 ($C^{1'}$), 81.11 (C^1), 119.30 (C^5), 133.69 (C^6), 160.21 (CHO), 178.50 (C^3). MS, *m/z*: 210.0896 $[M]^+$. Calc. for $C_{11}H_{14}O_4$: 210.0892.



(1R,2R,5S,6S,7S)-5-Hydroxymethyl-4-oxatricyclo-[5.2.1.0^{2,6}]dec-8-en-3-one **2e**. White crystals, mp 108-109ºC, $[\alpha]_D^{20}$-67.1º (*c* 1.0, $CHCl_3$), [ref[4]: mp 108-109ºC, $[\alpha]_D$-68.7º (*c* 0.6, $CHCl_3$)]. R_f 0.25 (hexane-EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 3432, 2976, 1755, 1193, 1028, 764. ^{1}H NMR ($CDCl_3$) δ: 1.46 (d, 1H, H^{10a}, 8.3 Hz), 1.53 (dt, 1H, H^{10b}, 8.3, 1.5 Hz), 2.34 (ddd, 1H, H^6, 7.1, 3.1, 1.2 Hz), 2.68 (dd, 1H, H^2, 7.1, 1.1 Hz), 2.90 (m, 1H, H^7), 2.96 (br.s, 1H, OH), 3.23 (m, 1H, H^1), 3.63 (dd, 1H, H^{11a}, 12.3, 4.6 Hz), 3.81 (dd, 1H, H^{11b}, 12.3, 3.0 Hz), 4.22 (ddd, 1H, H^5, 4.6, 3.1,

3.0 Hz), 6.16 (dd, 1H, H^8, 5.7, 2.8 Hz), 6.21 (dd, 1H, H^9, 5.7, 3.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 43.36 (C^{10}), 43.99 (C^6), 46.25, 47.23 (C^2, C^7), 48.77 (C^1), 64.25 (C^{11}), 84.23 (C^5), 137.09, 137.54 (C^8, C^9), 177.98 (C^3). MS, *m/z*: 180.0762 $[M]^+$. Calc. for $C_{10}H_{12}O_3$: 180.0786.



(1S,2R,5S,6S,7R)-5-Hydroxymethyl-4-oxatricyclo-[5.2.2.0^{2,6}]undec-8-en-3-one **2f**. White crystals, mp 80-82ºC, $[\alpha]_D^{20}$-8.0º (*c* 1.0, $CHCl_3$), [ref[5]: mp 80ºC, $[\alpha]_D$-10.5º (*c* 1.0, $CHCl_3$)]. R_f 0.3 (hexane-EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 3416, 2942, 1748, 1361, 1188, 1018, 720. ^1H NMR ($CDCl_3$) δ: 1.30 (m, 2H, H^{10}, H^{11}), 1.50 (m, 1H, H^{11}), 1.55 (m, 1H, H^{10}), 2.54 (dt, 1H, H^6, 10.0, 3.4 Hz), 2.70 (m, 1H, H^7), 2.83 (dd, 1H, H^2, 10.0, 3.4 Hz), 3.03 (m, 1H, H^1), 3.58 (dd, 1H, CH^{12a}, 12.3, 4.2 Hz), 3.78 (dd, 1H, CH^{12b}, 12.3, 2.8 Hz), 4.08 (m, 1H, H^5), 6.26 (dd, 1H, H^8, 7.6, 6.8 Hz), 6.32 (dd, 1H, H^9, 7.6, 6.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.34, 23.49 (C^{10}, C^{11}), 31.64 (C^1), 32.99 (C^7), 40.48 (C^6), 46.21 (C^2), 64.32 (C^{12}), 85.18 (C^5), 132.94 (C^8), 134.15 (C^9), 179.44 (C^3). MS, *m/z*: 194.0950 $[M]^+$. Calc. for $C_{11}H_{14}O_3$: 194.0943.

References

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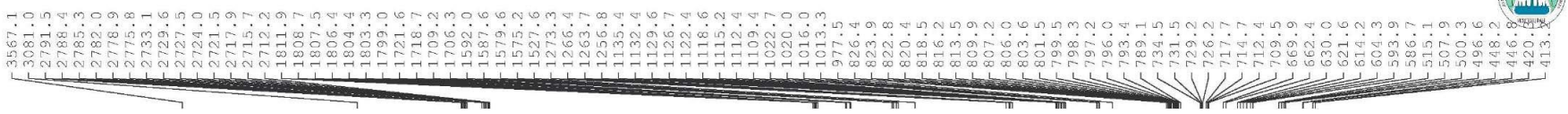

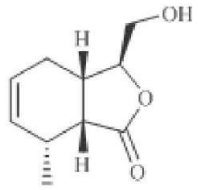

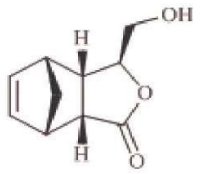

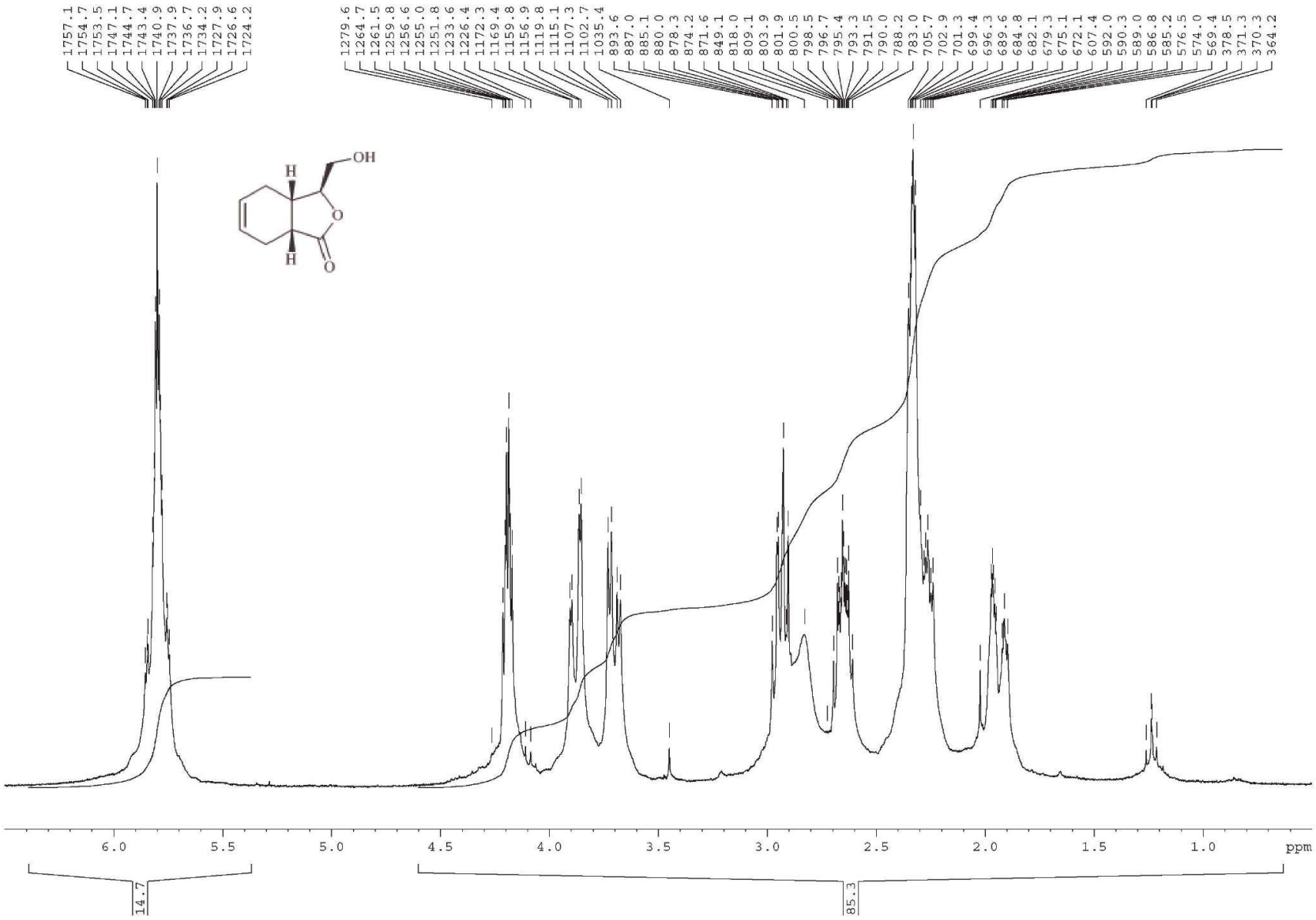

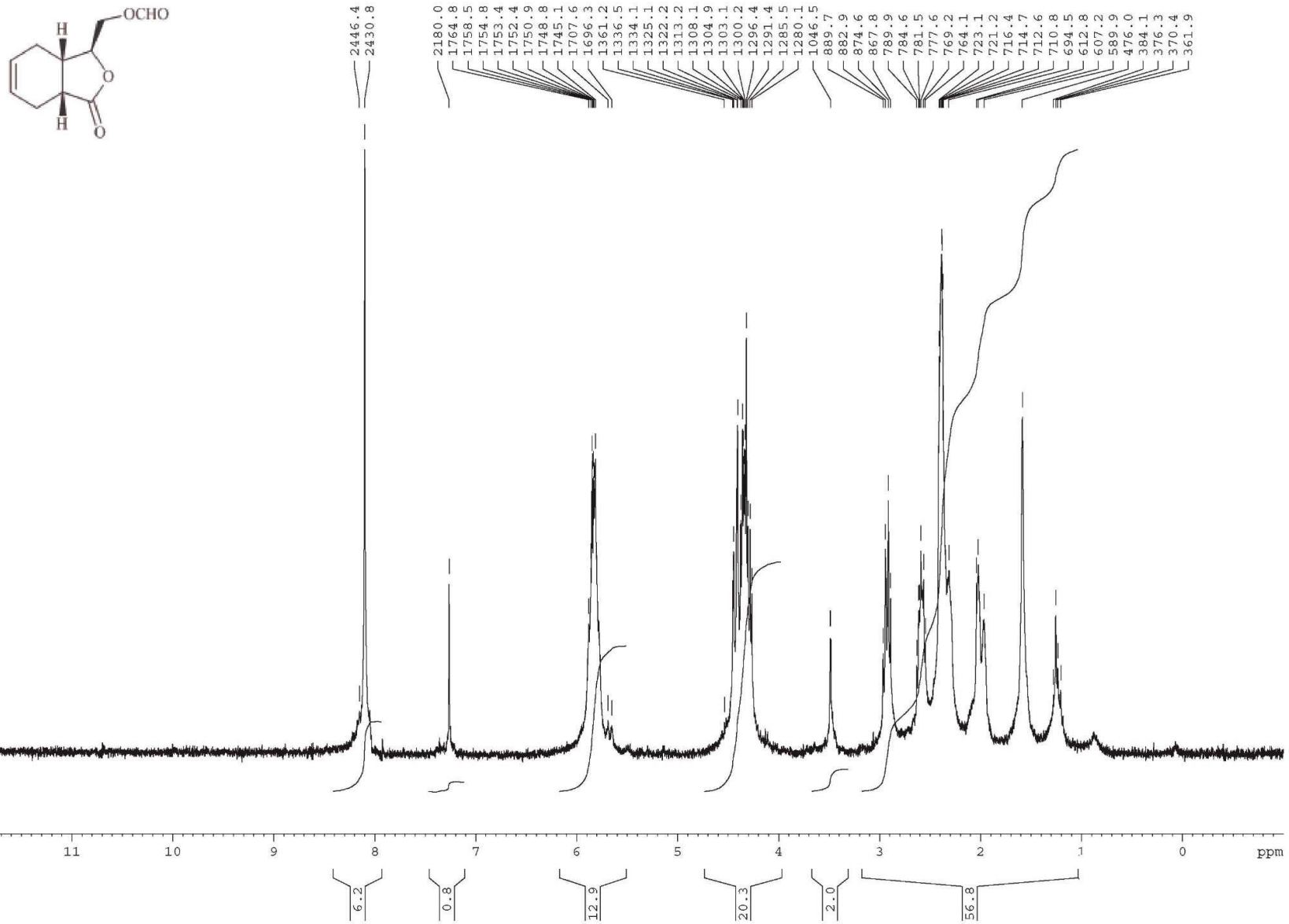

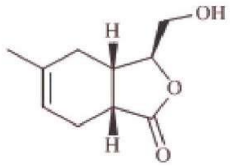

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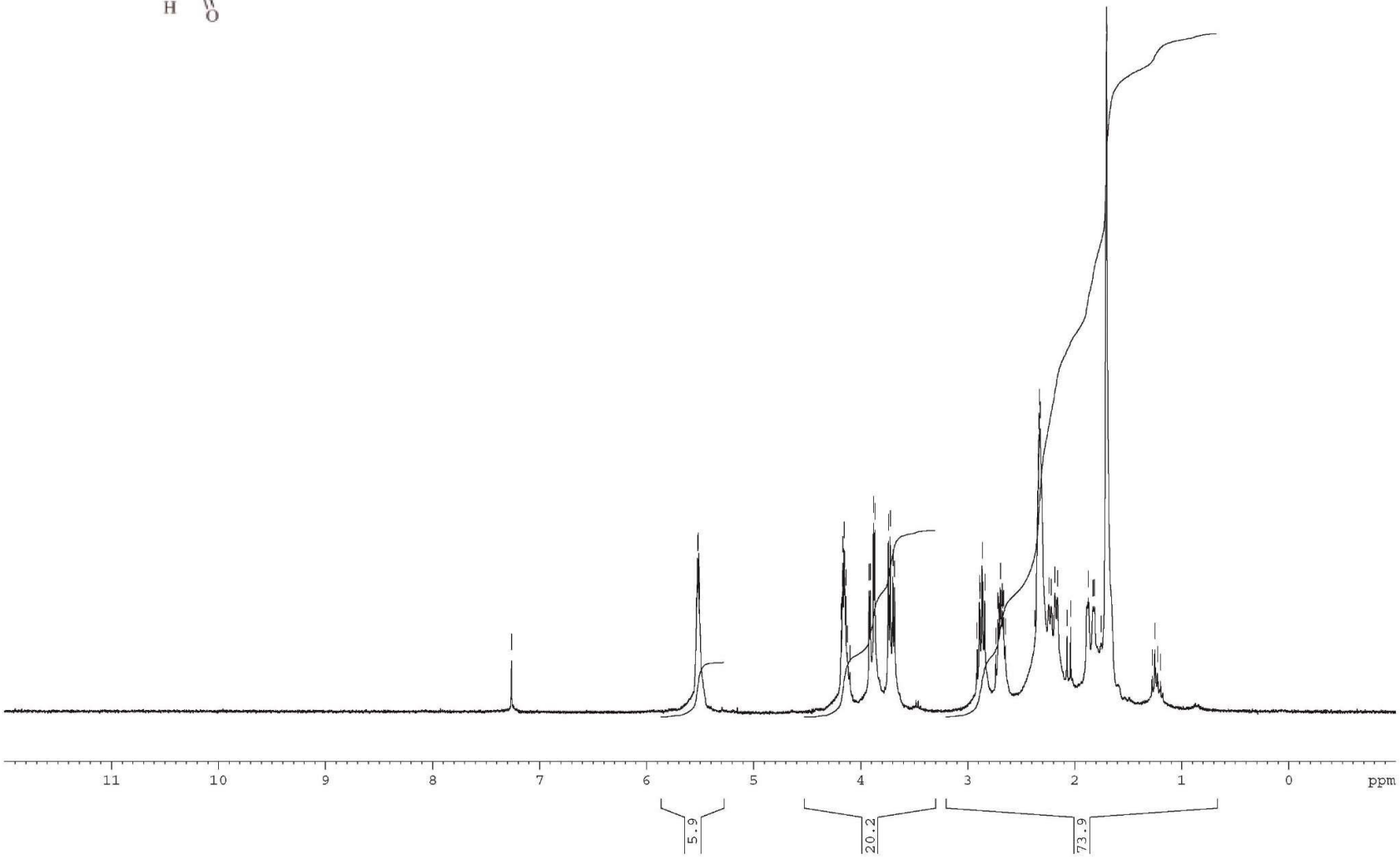

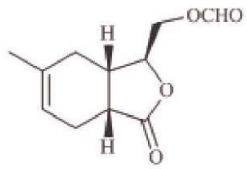

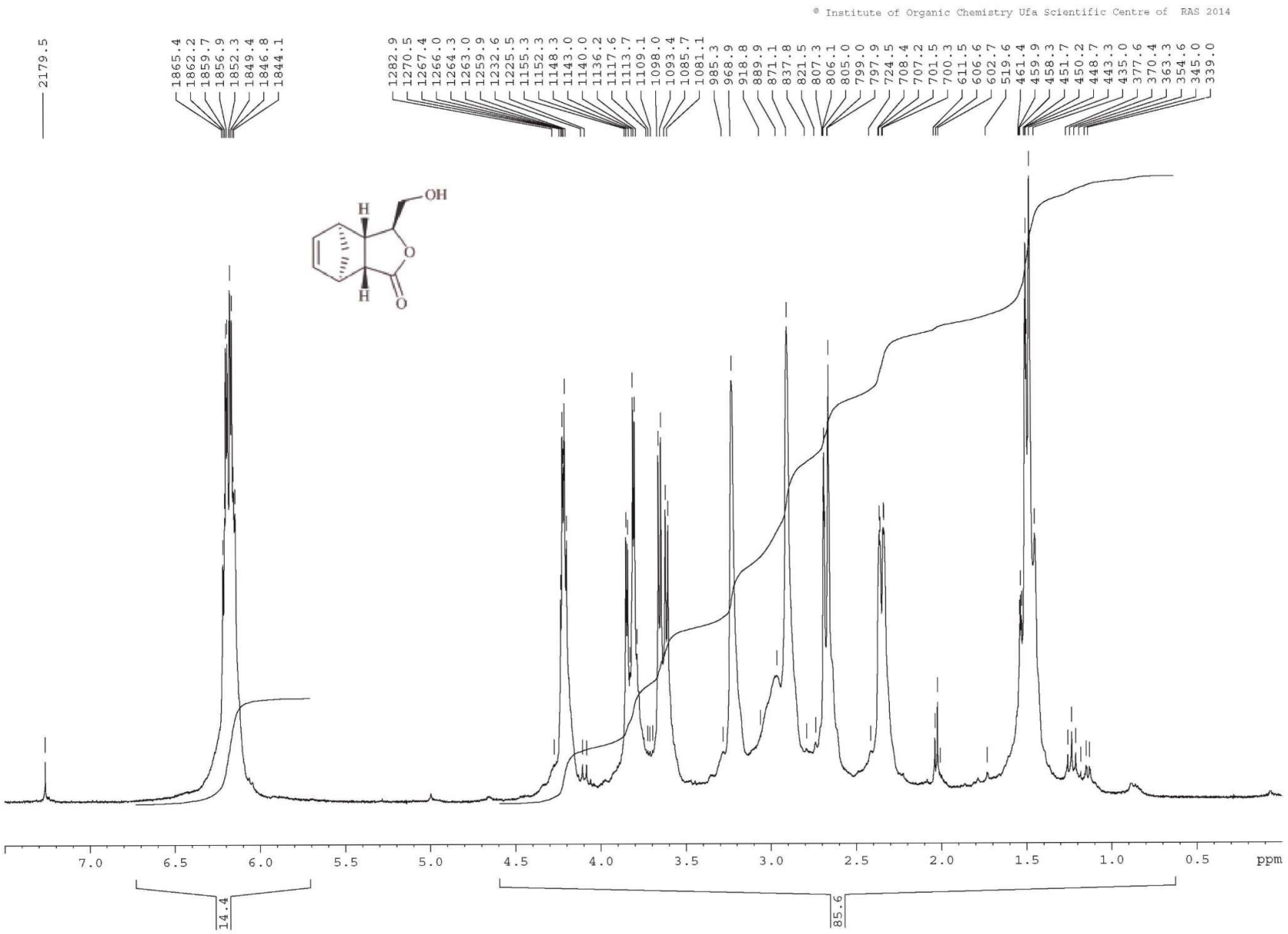

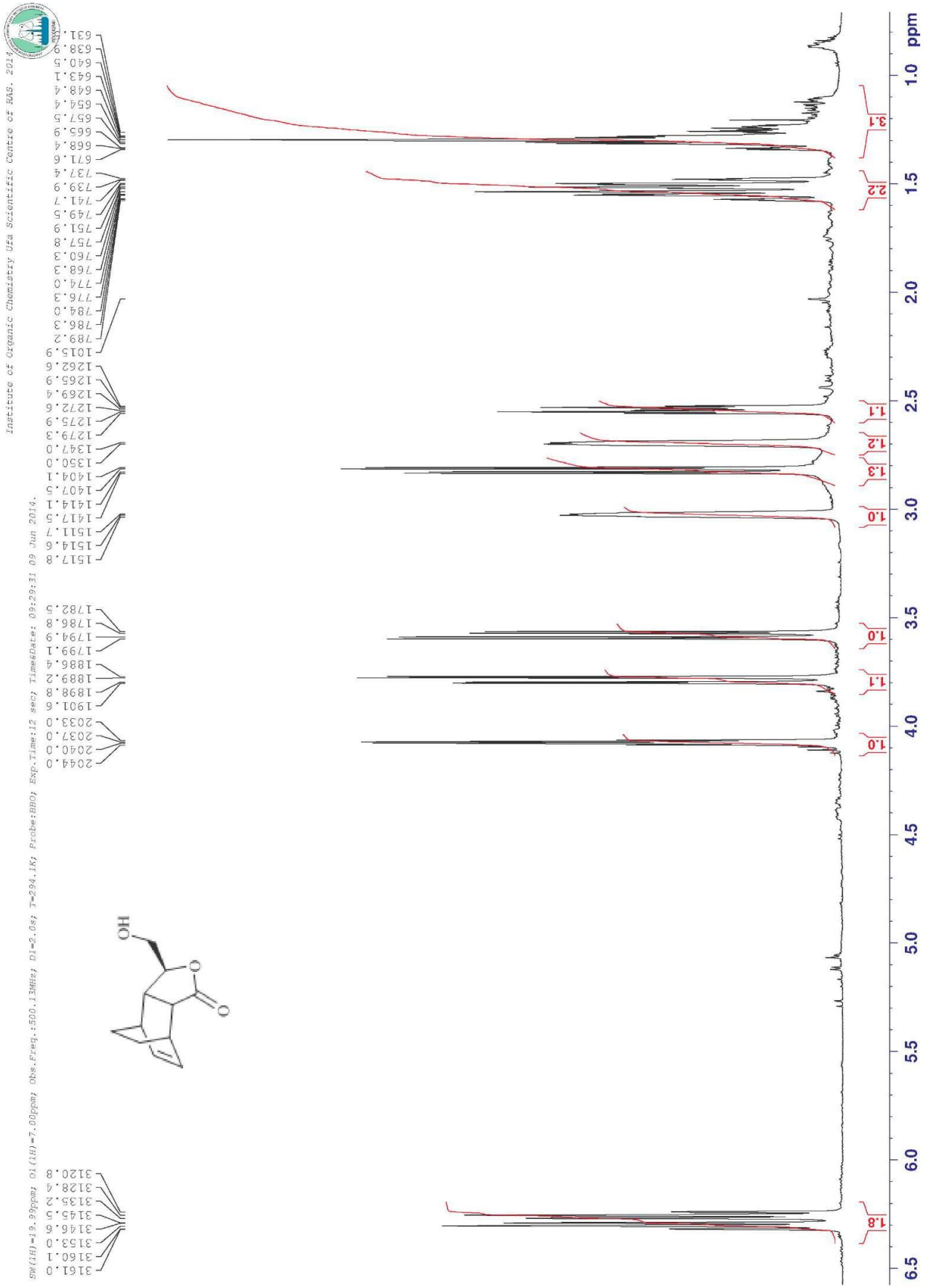
Institute of Organic Chemistry Ufa Scientific Centre of RAS. 2014
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OH
O
O
ppm